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RESEARCH ARTICLE

Comparison of the rare earth complexes iodides and polyiodides with biuret

Aleksandr D. Kornilov[1], Mikhail S. Grigoriev[2], Elena V. Savinkina[1,✉]

[1]MIREA – Russian Technological University (M.V. Lomonosov Institute of Fine Chemical Technologies), Moscow, 119571 Russia
[2]Frumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences, Moscow, 119071 Russia
✉Corresponding author, e-mail: savinkina@mirea.ru

Abstract

Objectives. *Currently, several hundred polyiodide compounds have been synthesized and structurally characterized, but so far, no formation patterns for certain polyiodide ions have been revealed. The purpose of this work is to continue the search for formation regularities of polyiodides, including polyiodides of lanthanide complexes.*
Methods. *Iodide and polyiodide of samarium complexes with biuret (BU),* $[Sm(BU)_4]I_3 \cdot BU \cdot 2H_2O$ *and* $[Sm(BU)_4][I_5][I]_2$*, were first synthesized and characterized by X-ray diffraction analysis and infrared spectroscopy, respectively.*
Results. *The obtained compounds complement the row of isostructural lanthanide (La–Gd) complexes. Structures of corresponding iodides and polyiodides were compared in detail. Both types of the compounds contain complex cations of the same composition; however, their structures differ significantly. The central atom coordination polyhedron can be described as a distorted square antiprism and a distorted dodecahedron, respectively. Even greater differences are observed in the outer sphere of complex compounds. The iodide compound crystals contain uncoordinated iodide ions, a biuret molecule and two water molecules. In the polyiodide compound, cations together with isolated* I^- *ions form a three-dimensional framework with the channels, in which linear* I_5^- *ions are united in infinite linear chains by weak interactions.*

Conclusions. *The replacement of an iodide ion with a polyiodide ion in complex compounds of lanthanides with BU leads to changes in both the inner sphere and the outer sphere of the cation complex, including the supramolecular level. The presence of iodine infinite linear chains in polyiodides allows expecting the presence of anisotropic electrical conductivity along this direction.*

Keywords: *lanthanides, samarium, iodide, polyiodide, crystal structure, anisotropy*

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НАУЧНАЯ СТАТЬЯ

Сравнение иодидов и полииодидов комплексов редкоземельных элементов с биуретом

А.Д. Корнилов[1], **М.С. Григорьев**[2], **Е.В. Савинкина**[1,✉]

[1]МИРЭА – Российский технологический университет (Институт тонких химических технологий им. М.В. Ломоносова), Москва, 119571 Россия
[2]Институт физической химии и электрохимии им. А.Н. Фрумкина Российской академии наук, Москва, 119071 Россия
✉Автор для переписки, e-mail: savinkina@mirea.ru

Аннотация

Цели. *В настоящее время синтезировано и структурно охарактеризовано несколько сотен полииодидных соединений, однако до сих пор не выявлено закономерностей образования тех или иных полииодид-ионов. Целью настоящей работы является продолжение поиска закономерностей образования полииодидов, в том числе полииодидов комплексов лантанидов.*
Методы. *Впервые синтезированы и охарактеризованы методами рентгеноструктурного анализа и инфракрасной спектроскопии, соответственно, иодид и полииодид комплексов самария с биуретом (BU) состава* $[Sm(BU)_4]I_3 \cdot BU \cdot 2H_2O$ *и* $[Sm(BU)_4][I_5][I]_2$.
Результаты. *Полученные соединения пополняют ряд изоструктурных комплексов лантанидов от La до Gd. Проведено детальное сравнение структур иодидных и полииодидных соединений. Установлено, что оба типа соединений содержат комплексный катион одного состава, однако его строение существенно различается в иодидных и полииодидных соединениях. Координационный полиэдр центрального атома можно описать как искаженную квадратную антипризму и искаженный додекаэдр, соответственно. Еще большие различия наблюдаются во внешней сфере комплексных соединений. Кристаллы иодидного соединения содержат некоординированные иодид-ионы, молекулу BU и две молекулы воды. В полииодидном соединении катионы вместе с одиночными ионами* I^- *образуют трехмерный каркас, в каналах которого находятся линейные ионы* I_5^-, *объединенные слабыми взаимодействиями в бесконечные линейные цепи.*

Выводы. *Замена иодид-иона на полииодид-ион в комплексных соединениях редкоземельных элементов с BU приводит к изменению как внутренней сферы катионного комплекса, так и внешней сферы, включая супрамолекулярный уровень. Присутствие бесконечных линейных цепей из атомов иода в структуре полииодидов комплексов лантанидов с BU позволяет ожидать наличие анизотропной электропроводности вдоль этого направления.*

Ключевые слова: *лантаниды, самарий, иодид, полииодид, кристаллическая структура, анизотропия*

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INTRODUCTION

One of the iodine features is its tendency to catenation, which results in the existence of numerous polyiodide ions [1]. At present, several hundred such compounds have been synthesized and structurally characterized, but so far, no regularities in the formation of certain polyiodide ions have been revealed. Even in the relatively simple $NMe_4I–I_2$ system, several unusual compounds have recently been discovered [2]. It is believed that large polyiodide anions should be stabilized by large cations, including complex ones. These include complexes of rare earth elements (REE). Several such compounds have been prepared, with only the polyiodides of REE complexes with urea (Ur) being systematically studied. $[Ln(Ur)_8][I_5][I_3]_2[I_2]$ (Ln = La–Nd, Sm–Dy), $[Ln(Ur)_7][I_3]_3$ (Ln = Ho, Er), $[Tm(Ur)_7][I_3]_3·2I_2$, and $[Ln(Ur)_6][I_3]_3$ (Ln = Yb, Lu, Sc) were isolated and structurally characterized [3–7]. It is noteworthy that the interaction of iodides of the above REEs (except Sc) with Ur produces isostructural compounds $[Ln(Ur)_4(H_2O)_4]I_3$ [8]. The interaction of REE iodides with biuret ($NH_2CONHCONH_2$, BU) and iodine resulted in formation of isostructural compounds $[Ln(BU)_4][I_5][I]_2$ (Ln = La, Nd, Gd) [9]. Regarding the corresponding iodide compounds, only two examples have been found in the literature. In the ErI_3–BU–H_2O system, an incongruently soluble compound of the composition $ErI_3·4BU$, characterized by infrared (IR) spectroscopy [10], was found, and the crystal structure of $[Gd(BU)_4]I_3·BU·2H_2O$ was studied [11].

The study aimed to synthesize and characterize iodide and polyiodide of a samarium complex with biuret and compare the obtained results with data on similar compounds of other REEs.

EXPERIMENTAL

Reagents produced in Russia were used.

Synthesis of $[Sm(BU)_4]I_3·BU·2H_2O$ (1). Samarium oxide (reagent grade, 2.45 g) was treated with hydroiodic acid (anal. grade), previously purified by distillation in the presence of hypophosphorous acid; the resulting solution was evaporated until crystallization began, then cooled. The resulting crystals of samarium iodide hydrate were mixed with biuret (pur., 1.45 g), at that, crystallization water was released. To homogenize the reaction mixture, a few more distilled water drops were added and the mixture was left for a month for crystallization. The resulting light-yellow prismatic crystals were separated and dried.

Synthesis of [Sm(BU)$_4$][I$_5$][I]$_2$ (2). Synthesis was carried out similarly, but in the presence of iodine (reagent grade, 5.36 g). The reaction product is black opaque crystals of the elongated prism form.

IR absorption spectra were recorded with an EQUINOX 55 FT-IR spectrometer (*Bruker*, Germany). Samples were prepared as KBr pellets for the range of 50–4000 cm^{-1} and as suspensions in Nujol placed on high density polyethylene (HDPE) windows for the range of 50–600 cm^{-1}.

The crystal structure of **1** was studied with a KAPPA APEX II autodiffractometer (*Bruker*, Germany)[1], MoKα radiation (0.71073 Å) at 100 K. The unit cell parameters were refined over the entire data set along with data processing.[2] Absorption corrections were introduced into the experimental reflection intensities.[3] The structure was solved by the direct method [12] and refined by the Least Squares method in the anisotropic approximation for all nonhydrogen atoms [13]. The H atoms of organic ligands are placed in geometrically calculated positions with isotropic temperature factors equal to 1.2 of equivalent isotropic factor of the N atom with which they are bonded. The H atoms of crystallization water molecules were localized on the difference Fourier synthesis of electron density and refined with limited O–H distances and H–O–H angles and with $U_{iso} = 1.5U_{eq}$(O). The atomic coordinates and thermal parameters for the crystal structure **1** were deposited at the Cambridge Crystallographic Data Center[4] under the CCDC 2120579 number. The main experimental parameters and crystallographic characteristics of compound **1** are given in Table 1.

RESULTS AND DISCUSSION

In the interaction of REE iodides with BU, polyiodides form more easily than the corresponding iodide complexes. Even if iodine is not added during the synthesis, the formation of not iodide, but polyiodide compounds often occur; in this case, the iodine necessary for the reaction form by the oxidation of I^{-} with atmospheric oxygen. In the case of samarium Sm, both compounds were obtained: [Sm(BU)$_4$]I$_3$·BU·2H$_2$O (**1**) and [Sm(BU)$_4$][I$_5$][I]$_2$ (**2**).

Table 1. Crystal data, data collection, and refinement parameters for structure **1**

Characteristic	Value
Empirical formula	$C_{10}H_{29}I_3N_{15}O_{12}Sm$
M	1082.53
Crystal system	Triclinic
Space group	*P*-1
a, Å	10.3152(3)
b, Å	12.7034(4)
c, Å	13.8461(4)
α, °	98.439(2)
β, °	103.658(2)
γ, °	112.284(1)
V, Å^3	1574.04(8)
Z	2
T, K	100(2)
D_{calc}, g cm^{-3}	2.284
μ(Kα), mm^{-1}	4.880
Scan range, °	2.84–29.96
Index ranges	$-14 \le h \le 14$; $-17 \le k \le 17$; $-19 \le l \le 19$
Crystal dimensions, mm	0.240 × 0.300 × 0.320
Reflections collected	33839
Independent reflections	9075
Number of parameters refined	382
Goodness of fit	1.093
Final *R*/*wR* [$I \ge 2\sigma(I)$]	0.0323/0.0704

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[1] APEX2, Bruker AXS Inc., Madison, Wisconsin, USA, 2006

[2] SAINT-Plus (Version 7.68), Bruker AXS Inc., Madison, Wisconsin, USA, 2007

[3] Sheldrick G. M. SADABS. Madison, Wisconsin (USA): Bruker AXS, 2008

[4] Cambridge Crystallographic Data Center, http://www.ccdc.cam.ac.uk/conts/retrieving.html

X-ray diffraction analysis of compound **1** was performed. The crystals contain: the $[Sm(BU)_4]^{3+}$ cation, coordination number is 8; uncoordinated iodide ions; a biuret molecule and two water molecules (Fig. 1). Structure **1** is isostructural to the analogous Gd compound [11]. However, the unit cell parameters determined in [11] differ from those given in Table 1. Parameters *a*, *b*, and *c* are close for both structures; however, for structure **1**, all angles are greater than 90°, while for the Gd compound, they are smaller. This difference is due to the rules for choosing a standard cell, which require that the diagonals of the cell faces are not shorter than its edges. When the edge *b* is replaced in the standard elementary cell of the Gd compound ($a = 10.374(4)$ Å, $b = 12.897(5)$ Å, $c = 13.854(5)$ Å, $\alpha = 71.46(3)°$, $\beta = 76.06(2)°$, $\gamma = 66.87(2)°$) with the diagonal of the face *ab*, the parameters of the nonstandard cell ($a = 10.374$ Å, $b = 12.994$ Å, $c = 13.854$ Å, $\alpha = 97.08°$, $\beta = 103.94°$, $\gamma = 114.11°$) are close to those given in Table 1 for the Sm compound.

It should be noted that in other previously studied Sm complex compounds with BU, $[Sm(BU)_4](ClO_4)_3$ [14] and $[Sm(BU)_4](NO_3)_3$ [15], outer-sphere BU molecules are absent.

Each BU molecule is coordinated through two oxygen atoms. The shape of the coordination polyhedron, as for the Gd compound, is a distorted square antiprism. The Sm–O bond lengths are 2.358(3)–2.442(3) Å. It can be noted that the inner-sphere BU molecules are in the cis configuration, while the outer-sphere molecules are in the trans configuration stabilized by an intramolecular H bond. In this case, the inner-sphere BU molecules are not planar, in contrast to the outer-sphere one: the angles between the OCN planes of two fragments of BU molecules are 5.82°–15.41° and 2.02°, respectively. In addition, for three ligands, a noticeable rotation of the Sm–O bonds about the mean plane of the ligand is observed, the torsion angles Sm–O–O–C are 147°–157° (for the fourth molecule, about 176°). The outlet of the Sm atom from the planes of BU molecules is almost 1 Å. It should be noted that the single planar Sm–Bu fragment does not form H bonds with the outer-sphere BU molecules and water (it participates only in H bonds with the neighboring complex cation). Apparently, this favors the greater electron density delocalization along the chelate cycle [16, 17].

In structure **1**, the outer-sphere BU molecules are located among the complex cations and are united with them, as well as with crystallization water molecules and iodide ions, by H bonds. In this case, layers of complex cations and outer-sphere BU molecules can be seen in the structure; these layers are interconnected by water molecules (Fig. 2). The formation of hydrogen bonds of the N–H...O and O–H...O types leads to the formation of a three-dimensional framework, which is very characteristic of N,O-containing compounds [18–20].

For compound **2**, it was not possible to grow crystals suitable for X-ray diffraction analysis,

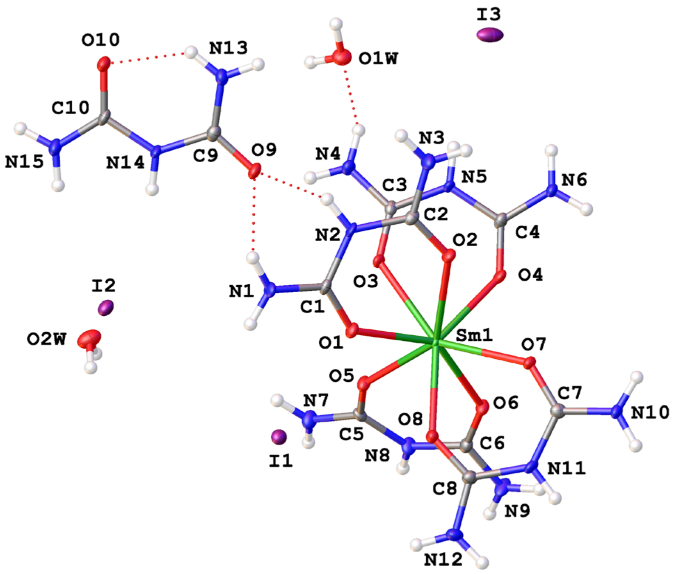

Fig. 1. Molecular structure of $[Sm(BU)_4]I_3·BU·2H_2O$ (**1**); ellipsoids 50%. H-bonds are shown with dotted lines.

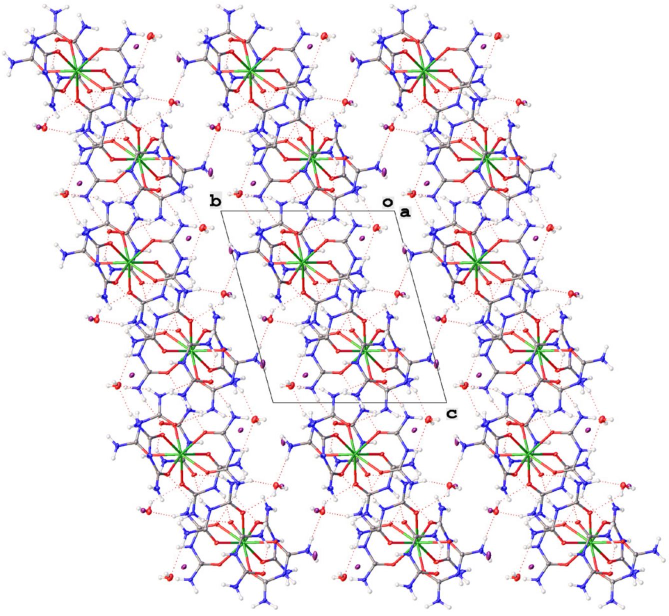

Fig. 2. Crystal packing of $[Sm(BU)_4]I_3·BU·2H_2O$ (**1**).

as well as to obtain high-quality powder diffraction patterns. Therefore, it was studied by IR spectroscopy in the region from 40 to 4000 cm^{-1}. The main bands and their assignment for **2** and similar La, Nd, and Gd compounds are given in Table 2.

The ν(CO) frequency shifts towards lower values and δ(NH_2) towards higher values indicates that BU is coordinated to Sm via O atoms. The bands at 71 and 95 cm^{-1} in the compound **2** spectrum are assigned to δ(I–I–I), and at 144 cm^{-1}—to ν(I–I)

Table 2. IR spectra of $[Ln(BU)_4][I_5][I]_2$

Biuret [17]	Ln				Assignment
	La [9]	Nd [9]	2 [this work]	Gd [9]	
–	73 95	67 95	71 95	70 94	δ(I–I–I)
	144	144	143	143	ν(I–I)
	200 213	198 218	197 215	195 215	δ(OMO) + ν_s(MO)
	–	242	241	250	δ(OMO)
	302	295 309	294	282 300	δ(OMO) + ν_{as}(MO)
	399 421 444	395 442 457	397 417 445	398 415 446	ν_{as}(MO)
	496 522	482	490 522	487	π(MOC) + ρ_r(NH_2)
	591	582	582	582	π(NH) + δ(MOC)
710	643	648	647	650	δ(C=O)
770	770	769	769	770	δ(C–NH_2)
946	945	944	944	948	ν(CN) + ν(C–NH_2)
1323	1330	1327	1326	1332	δ(NH)
1423 1499	1481	1480	1480	1487	ν(CN) + ν(C–NH_2)
1585	1608	1605	1607	1610	δ(NH_2)
1719	1698	1688	1696	1700	ν(CO)
3254	3209 3259	3238 3272	3208 3269	3211 3264	ν_s(NH_2)
3415	3405	3408	3388	3407	ν_{as}(NH_2)

of polyiodide chains [21]. It should be noted that the compound **2** IR spectrum almost completely coincides with the spectra of previously studied Ln, Nd, and Gd polyiodides [9], especially in the long-wavelength region, where the characteristic vibrations of polyiodide particles are located.

Based on the isostructurality of $[Ln(BU)_4][I_5][I]_2$ (Ln = La, Nd, Gd) [9] and analysis of IR spectra (especially in the long wavelength region, which is extremely sensitive to the structure of the polyiodide anion), it can be assumed that the Sm compound also belongs to this isostructural series.

Polyiodide compounds, like iodide compounds, contain the complex cation $[Ln(BU)_4]^{3+}$, but its structure differs from that of the cation in iodide compounds. Pairs of BU molecules and Ln atoms in $[Ln(BU)_4][I_5][I]_2$ are located in two almost perpendicular planes. The outlet of Ln atoms from the planes of BU molecules does not exceed 0.1 Å. The Ln coordination polyhedron can be described as a distorted dodecahedron.

The absence of water can be explained by the fact that poorly hydrated polyiodide ions are displaced from the aqueous medium into the solid phase, preventing water molecules from being fixed in the crystal lattice. This phenomenon can be used for further synthesis of anhydrous REE compounds, which are widely used [22].

Stabilization of polyiodide anions can be realized in two ways: polyiodide ions can be included in a supramolecular framework built by cations, or they themselves can form a framework, and cations will be located in its cavities [23]. In the previously studied polyiodides of amide complexes, the second variant was observed. However, in the case of BU compounds, it is the cations (together with single I^- ions) that form a three-dimensional framework, in the channels of which there are linear I_5^- ions, united by weak interactions into infinite linear chains, which should cause the presence of anisotropic electrical conductivity along this direction [9].

CONCLUSIONS

An analysis of the iodides and polyiodides structure of REE complexes with BU showed that they contain $[Ln(BU)_4]^{3+}$ cationic complexes of the same composition but different structures. The complexes differ significantly in the mutual arrangement of the BU ligands and in the coordination polyhedra. Even greater differences can be noted in the outer-sphere of complex compounds. Iodide ions, water molecules, and uncoordinated BU, combined with complex cations by hydrogen bonds are in the outer-sphere of iodide compounds. In the outer-sphere of polyiodides, there are iodide ions, which together with complex cations form a three-dimensional framework, and pentaiodide ions, united by weak contacts into infinite linear chains. At the same time, there are no noticeable interactions between the polyiodide chains and the rest of the complex compound.

Thus, the replacement of the iodide ion by the polyiodide ion in REE–BU complex compounds leads to the change in both the inner-sphere and the outer-sphere of the cationic complex, including the supramolecular level.

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Authors' contributions

A.D. Kornilov – synthesis and analysis of compounds, IR spectroscopy;

M.S. Grigoriev – X-ray diffraction analysis;

E.V. Savinkina – overall supervision, literature review, analysis of results, and writing the text of the article.

The authors declare no conflicts of interest.

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About the authors:

Aleksandr D. Kornilov, Master Student, N.A. Preobrazhensky Department of Chemistry and Technology of Biologically Active Compounds, Medicinal and Organic Chemistry, M.V. Lomonosov Institute of Fine Chemical Technologies, MIREA – Russian Technological University (86, Vernadskogo pr., Moscow, 119571, Russia). E-mail: sashakornilov@bk.ru. https://orcid.org/0000-0001-6164-8650

Mikhail S. Grigoriev, Dr. Sci. (Chem.), Chief Researcher, Head of the Laboratory of Analysis of Radioactive Materials, A.N. Frumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences (31, b. 4, Leninskii pr., Moscow,119071, Russia), E-mail: grigoriev@ipc.rssi.ru. ResearcherID U-8572-2017, https://orcid.org/0000-0002-6363-5535

Elena V. Savinkina, Dr. Sci. (Chem.), Professor, A.N. Reformatskii Department of Inorganic Chemistry, M.V. Lomonosov Institute of Fine Chemical Technologies, MIREA – Russian Technological University (86, Vernadskogo pr., Moscow, 119571, Russia). E-mail: savinkina@mirea.ru. Scopus Author ID 8419176500, ResearcherID G-2949-2013, https://orcid.org/0000-0002-2088-5091

Об авторах:

Корнилов Александр Денисович, магистрант кафедры технологии биологически активных соединений, медицинской и органической химии им. Н.А. Преображенского Института тонких химических технологий им. М.В. Ломоносова ФГБОУ ВО «МИРЭА – Российский технологический университет» (119571, Россия, Москва, пр-т Вернадского, д. 86). E-mail: sashakornilov@bk.ru. https://orcid.org/0000-0001-6164-8650

Григорьев Михаил Семёнович, д.х.н., главный научный сотрудник, заведующий лабораторией анализа радиоактивных материалов, Институт физической химии и электрохимии им. А.Н. Фрумкина Российской академии наук (119071, Россия, Москва, Ленинский проспект, 31, корп. 4). E-mail: grigoriev@ipc.rssi.ru. ResearcherID U-8572-2017, https://orcid.org/0000-0002-6363-5535

Савинкина Елена Владимировна, д.х.н., профессор кафедры неорганической химии им. А.Н. Реформатского Института тонких химических технологий им. М.В. Ломоносова ФГБОУ ВО «МИРЭА – Российский технологический университет» (119571, Россия, Москва, пр-т Вернадского, д. 86). E-mail: savinkina@mirea.ru. Scopus Author ID 8419176500, ResearcherID G-2949-2013, https://orcid.org/0000-0002-2088-5091

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